

# THERMAL DeNO<sub>x</sub>: A COMMERCIAL SELECTIVE NONCATALYTIC NO<sub>x</sub> REDUCTION PROCESS FOR WASTE-TO-ENERGY APPLICATIONS

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## ABSTRACT

The THERMAL DeNO<sub>x</sub> process has been licensed by Exxon Research and Engineering Company for use in over sixty commercial installations. Two installations are waste incinerators—300 tons<sup>1</sup>/day refuse and 360 tons/day sludge (consisting of three trains each 120 tons/day), both in the Los Angeles Basin. The process offers the advantages of high deNO<sub>x</sub>, low investment and low risk of downstream equipment fouling. This paper describes the technical and economic advantages for application of the process to waste incinerators.

## INTRODUCTION

THERMAL DeNO<sub>x</sub>, a selective noncatalytic NO<sub>x</sub> reduction process, was invented just over 12 years ago and is a patented process of Exxon Research and Engineering Co. [1, 2]. The process involves the injection of ammonia (NH<sub>3</sub>) into the high temperature flue gas in the 1600–2200°F (870–1200°C) temperature range. The original applications were in Japan beginning in

1974, where deNO<sub>x</sub> performance ranging up to 65% was achieved. Total commercial applications to date number over 60, as shown in Table 1, and commercial performance in excess of 80% deNO<sub>x</sub> has been achieved utilizing recently improved technology.

The type of installations to which the process has been applied are wide ranging including gas and oil-fired steam boilers, utility boilers, process heaters, municipal incinerators, oil field steam generators and a glass melting furnace. Tests on flue gas generated by coal combustion have demonstrated the applicability of the process to coal-fired utility boilers, and two coal-fired utility boilers are currently under license in Germany.

One of the earliest applications of this process was a test conducted at the Kobe City, Japan incinerator during December, 1975. Even though this test involved the use of older technology and no attempt was made to optimize NO<sub>x</sub> reduction, greater than 50% deNO<sub>x</sub> was achieved. In another test, deNO<sub>x</sub> efficiency of greater than 85% was achieved [3]. Current units under construction include a 300 tons/day municipal refuse incinerator and a 360 tons/day sludge-fired incinerator.

Recently, development of a fundamental kinetic model of the process chemistry has significantly expanded the understanding of process variable interactions [4]. This model, along with a knowledge of

<sup>1</sup> All tons referred to are U.S. tons, not metric tons, unless otherwise noted. One U.S. ton equals 907.2 kg.

TABLE 1 THERMAL DeNO<sub>x</sub> EXPERIENCE SUMMARY

|  | Installed | Construction Phase | Design Phase |
|--|-----------|--------------------|--------------|
| Japanese Industrial Boilers                    | 4         |                    |              |
| Japanese Utility Boilers                       | 5         |                    |              |
| Japanese Petroleum Heaters                     | 4         |                    |              |
| Japanese Municipal Incinerator (Demonstration) | 1         |                    |              |
| California Oil Field Steamer (Demonstration)   | 1         |                    |              |
| California Flat Glass Melting Furnace          | 1         |                    |              |
| California Petroleum Heaters                   | 30        |                    |              |
| California Utility Boiler                      | 1         |                    |              |
| California Industrial Boilers                  | 3         |                    | 1            |
| California Incinerators                        | 1         | 1                  | 1            |
| California Oil Field Steamers (Commercial)     | 5         |                    |              |
| California Wood-Fired Boilers                  | 1         |                    | 1            |
| German Coal-Fired Utility Boilers              | 2         |                    |              |

other physical factors affecting performance, is used to accurately predict performance and NH<sub>3</sub> breakthrough for any type of fired equipment.

Most of the applications to date have involved positioning an array of injector pipes or an injection grid within the flue gas stream at the proper flue gas temperature for injecting NH<sub>3</sub> [5, 6]. Location of the grid is critical to achieving optimum performance; but too often, especially in retrofit situations, the optimum position is inaccessible. Because of this, and to account for lower than optimum temperature at reduced loads, the simultaneous injection of hydrogen has been used to extend the process effectiveness to lower flue gas temperatures. However, recent development of novel injector designs along with techniques to better assess their effectiveness has virtually eliminated the use of grids and their associated problems, and the use of hydrogen [7-9]. These developments coupled with the kinetic model comprise the improved technology.

The improved technology offers the following major advantages:

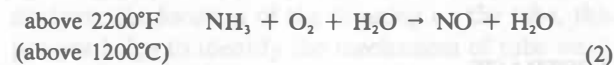
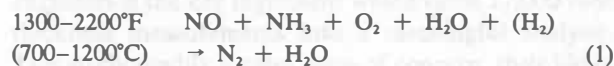
- (a) higher performance
- (b) better load following without hydrogen
- (c) grid-less injectors
- (d) lower capital investment

Field tests of the novel injector designs located optimally have revealed substantially greater performance capability of 70% to over 80% deNO<sub>x</sub>. In effect, the process now offers performance approaching that of competing catalytic processes for a wide range of fired

equipment, while also achieving even greater cost effectiveness through the combination of lower investment and higher performance.

### KINETIC MODEL EXPANDS PROCESS UNDERSTANDING

THERMAL DeNO<sub>x</sub> is a noncatalytic process based on the gas phase homogeneous reaction between the NO<sub>x</sub> in flue gas and NH<sub>3</sub> which produces nitrogen and water [1]. In general, NH<sub>3</sub> is injected into the hot flue gas by means of either air or steam carrier gas at a point in the flue specifically selected to provide optimum reaction temperature and residence time. The following two reactions govern the overall process:



As indicated by Eq. (1), hydrogen (H<sub>2</sub>) can be injected along with NH<sub>3</sub> to extend the effectiveness of the deNO<sub>x</sub> reaction down to the range of 1300°F (700°C).

Equations (1) and (2) summarize the overall effect of the deNO<sub>x</sub> reaction, but they do not reveal the complexity of interaction of numerous intermediate chain branching reactions involving certain key free radicals. This complex chemical mechanism includes a total of 31 significant reactions. Rate equations, involving these thirty-one reactions, have been developed using both reliable published data as well as experimental data to yield a fundamental kinetic model of the process chemistry. Calculated results with the model correlate with an extensive set of experimental data within ± 7% [2].

The kinetic model has been successful in assessing the process capability through a more precise calculation of the interaction of flue gas constituents and physical conditions including temperature, time, initial NO<sub>x</sub>, NH<sub>3</sub>/NO<sub>x</sub> ratio, O<sub>2</sub>, H<sub>2</sub>O and free radicals. This technology has enabled extension of the temperature window using NH<sub>3</sub> alone from under 1600°F (870°C) to over 2200°F (1200°C) under certain conditions of the other kinetic parameters. The model can be used to determine the optimum amount of NH<sub>3</sub> which

should be injected at a given location. Also, the model permits accurate prediction of unreacted ammonia.

The kinetic model calculations represent kinetic limit performance for the process and this may be lowered in a real system due to one or more of the engineering design or unit specific parameters including mixing, carrier rate, flue gas temperature and velocity gradients, and staged injection. The influence of each of these parameters has been the subject of considerable research and development, and some work in this area is being continued. Mixing effectiveness of grid injectors has been increased such that it is possible to achieve 95–100% of the kinetic limit performance [6]. Wall injector mixing can now be optimized for a specific geometry by utilizing a recently field-validated three-dimensional flow modeling technique [10, 11].

### WALL INJECTORS REPLACE INJECTION GRIDS

The original applications involved positioning an injection grid within the flue gas stream at the proper flue gas temperature for injecting a mixture of  $\text{NH}_3$  and carrier steam or air [5, 6]. Sometimes, multiple grids and/or hydrogen were employed to achieve some load following, but this increased the complexity and cost of the installation. Also, many potential users questioned the long term operability of the grid, particularly in corrosive, erosive or heavy fouling flue gas streams such as occur with refuse-firing. In most applications today, the injection grids are being superseded by wall injectors which consist of large jets located at or near the boundary walls of the injection zone.

The wall injectors are simple and relatively inexpensive, but require careful design and placement in order to achieve optimum process results. They are not subject to overheating upon loss of carrier, nor do they face corrosive attack and/or collection of fuel ash deposits such as may result from firing heavy fuel oil, coal or refuse. These factors permit location of the injectors at the optimum flue gas temperature even within the combustion zone of fired equipment. To accommodate turndown operation, two sets of injectors may be used with very little impact on overall cost. Through proper location of the injectors to cover the load range, the necessity of hydrogen injection to promote low flue gas temperature performance is eliminated. In addition, if flue gas temperatures during operation of a unit are substantially different from

those anticipated in the design, the wall injectors may be relocated either onstream or during a short outage.

### FLOW MODELING PERMITS OPTIMIZATION OF WALL INJECTORS

While the wall injectors offer substantial benefits over injection grids, they also pose a challenging problem to achieve adequate mixing especially in very large fired equipment. This has spurred development of a three-dimensional, turbulent flow modeling technique [11]. Use of this technique coupled mathematically with the kinetic model, permits the direct calculation of  $\text{deNO}_x$  performance for any geometry and flow condition.

The use of this modeling technique in predicting  $\text{deNO}_x$  performance is shown graphically for a 300 tons/day municipal refuse incinerator/boiler and a 120 tons/day sludge-fired incinerator/boiler.

The municipal refuse incinerator shown in Fig. 1 is a stoker-fired unit which utilizes a reciprocating grate. Flue gases from the burning refuse travel upward through a combustion chamber into the superheater and steam generating tube bank, then down through an economizer, and exhaust through a scrubber and baghouse.

The ammonia injectors are arranged in two zones at two elevations of the combustion chamber. Zone 1 is planned for high loads and Zone 2 for lower loads.

Calculated performance results at 100% load are shown in Fig. 2 for one-fourth of the flue gases. Here, combustion chamber temperatures vary from approximately 1830°F (1000°C) to 1550°F (840°C) over the reaction zone at full load. Predicted performance results are well in excess of 70%  $\text{deNO}_x$  for this installation, reducing the  $\text{NO}_x$  from an initial level of 204 vppm to less than 60 vppm (average).

The sludge incinerator shown in Fig. 3 utilizes a circulating fluidized bed type combustor. Combustion is completed in the furnace shaft after which primary particulate removal is achieved. The cleaner flue gases then pass consecutively through a superheater, economizer, multiclone and air preheater. Flue gas exits the heat recovery section and is sent to a dry scrubber and baghouse before being sent to the stack.

Two zones of injectors are provided for this boiler, one in the furnace shaft and one downstream of the primary particulate removal. Due to the low flue gas temperature of 1550°F (840°C), it is necessary to inject a mixture of  $\text{NH}_3$  and hydrogen to achieve the necessary reaction efficiency.  $\text{NO}_x$  reduction required to

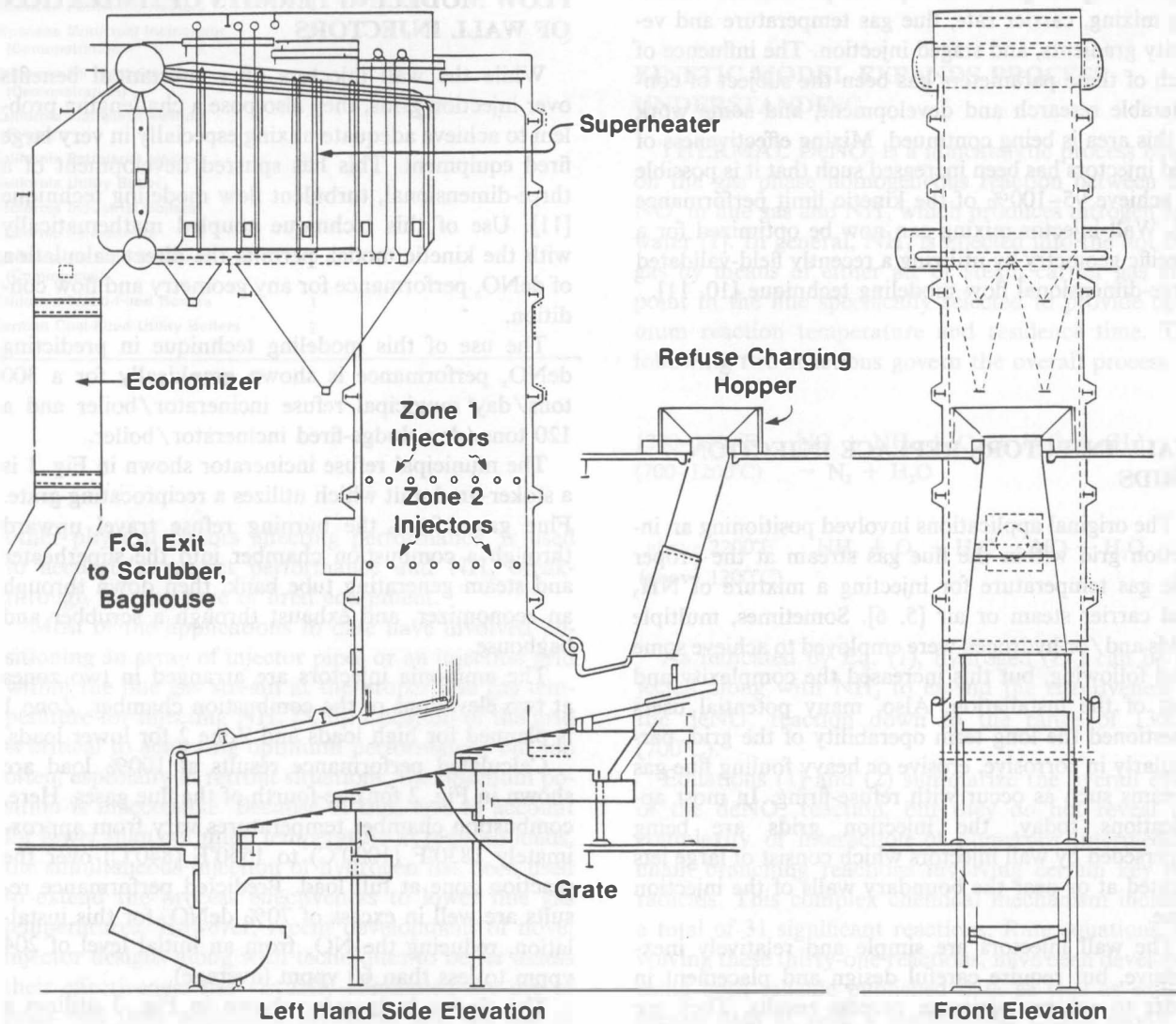


FIG. 1 THERMAL DeNO<sub>x</sub>—300 tons/day MUNICIPAL REFUSE INCINERATOR

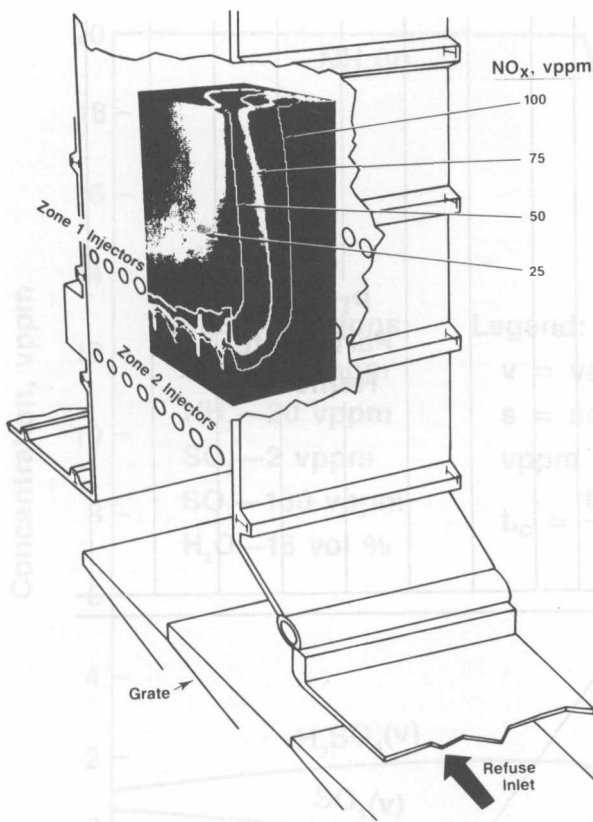


FIG. 2 ILLUSTRATION OF DeNO<sub>x</sub> REACTION MODELING RESULTS FOR 300 tons/day MUNICIPAL REFUSE INCINERATOR

meet permit conditions is approximately 46% and this is well within the process capability limit. Figure 4 illustrates the effectiveness of mixing of a zone of injectors located at the wall of the furnace shaft.

### POTENTIAL USER CONCERNS

One of the major concerns over use of ammonia injection in reducing NO<sub>x</sub> generated by refuse combustion is the effect of residual NH<sub>3</sub> in the flue gas. Residual NH<sub>3</sub> may react with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloric acid (HCl) to form ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>], ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>), and ammonium chloride (NH<sub>4</sub>Cl). These salts can contribute to fouling and/or plume formation if present in sufficient quantities. Also, there is minimal industry experience on the effect of ammonia or ammonium salts on scrubbers and baghouses, and thus this is a potential problem area.

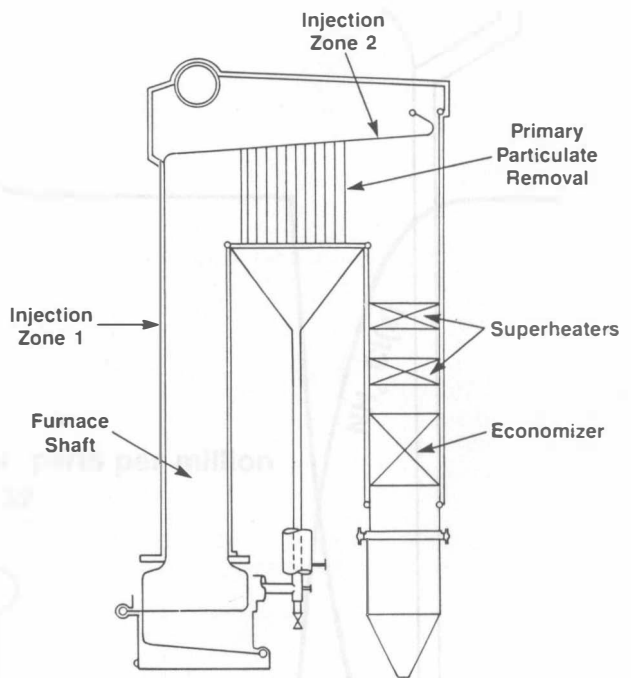


FIG. 3 THERMAL DeNO<sub>x</sub>—120 tons/day SLUDGE-FIRED INCINERATOR  
(Courtesy of Babcock & Wilcox, a McDermott Company)

The three potential ammonium salts have very different characteristics. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is a dry salt with a neutral pH. Its small particle size of 1–3 μm further reduces the fouling tendency of this compound. NH<sub>4</sub>HSO<sub>4</sub>, on the other hand, is an acidic hygroscopic compound with a relatively low melting point—as low as 266°F (130°C). When present, this compound can contribute to significant fouling and corrosion in low temperature heat recovery equipment.

NH<sub>4</sub>Cl is a dry, neutral pH, white salt which forms at very low temperature on the order of 250°F (120°C) or less. This salt can contribute to a visible plume when present in sufficient concentrations.

On the positive side, one similar characteristic of all three ammonium compounds is their high water solubility. This makes deposit removal by water washing relatively straightforward.

Equilibrium reactions in the low temperature flue gas are shown in Fig. 5 for a typical refuse-fired incinerator. Due to the low sulfur content of the refuse, the amount of H<sub>2</sub>SO<sub>4</sub> formed is only 2 vppm. This reacts with NH<sub>3</sub> at about 390–360°F (200–180°C) to produce 2 vppm of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. At approximately 250°F (120°C), the remaining NH<sub>3</sub> begins reacting with HCl, forming NH<sub>4</sub>Cl. This reaction is essentially complete at 190°F (90°C) when all of the residual NH<sub>3</sub> is reacted.

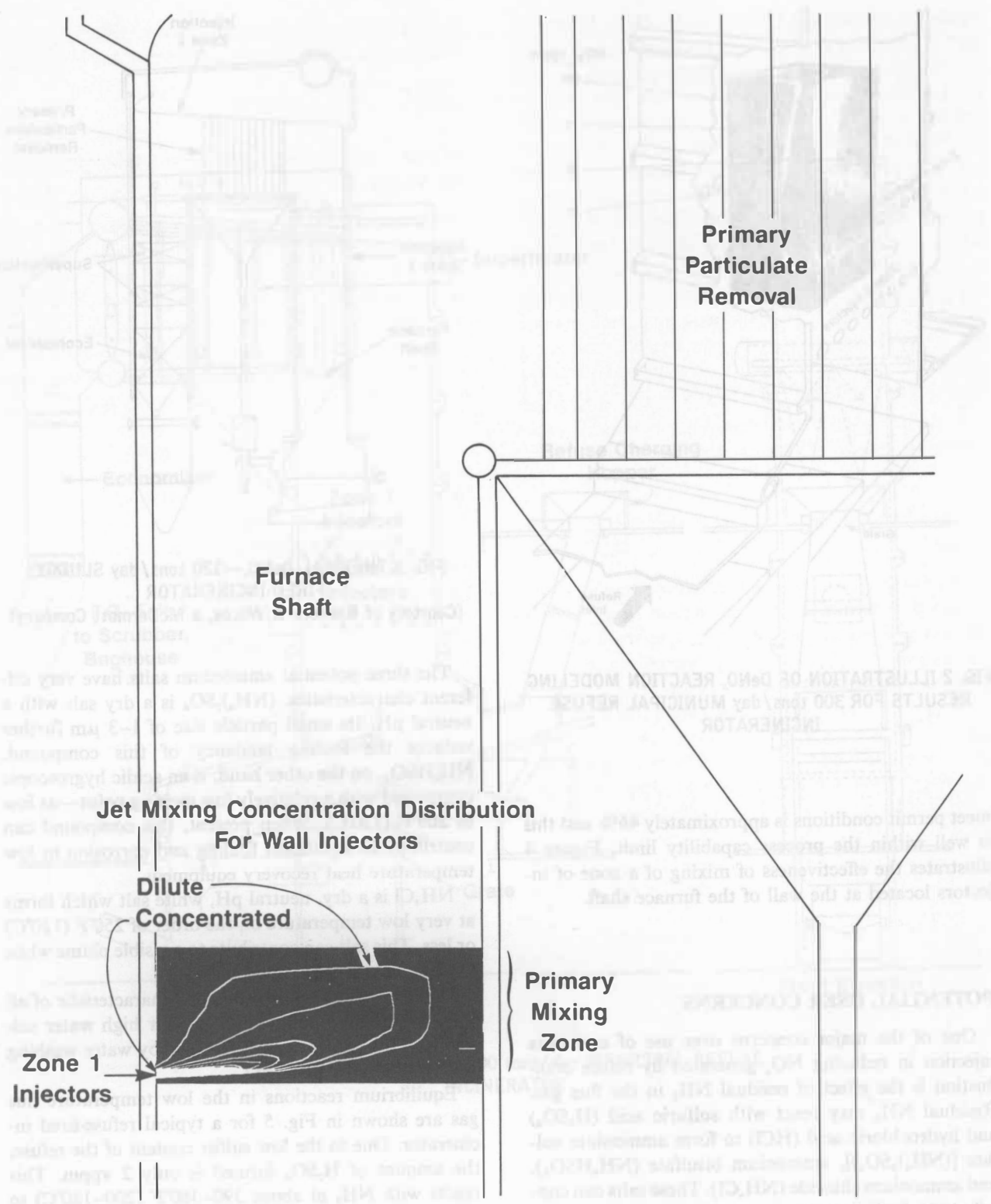


FIG. 4 ILLUSTRATION OF DeNO<sub>x</sub> INJECTOR MIXING FOR 120 tons/day SLUDGE-FIRED INCINERATOR



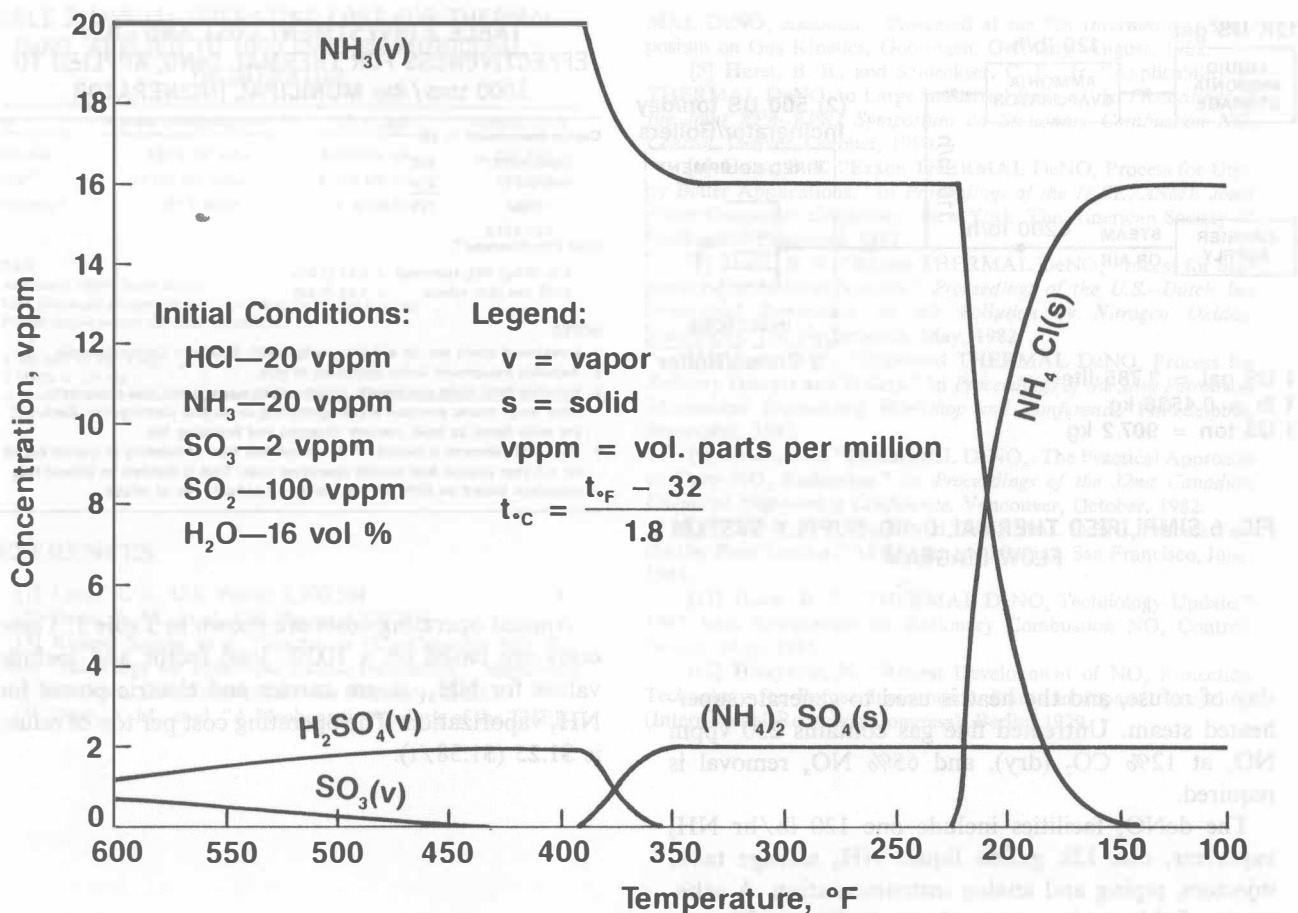


FIG. 5 EQUILIBRIUM REACTIONS IN COOLED FLUE GASES FROM COMBUSTION OF MUNICIPAL REFUSE

The impact of  $(\text{NH}_4)_2\text{SO}_4$  is expected to be negligible due to its small quantity and innocuous nature. It is anticipated that the additional particulate which it represents will not be detectable compared to the much larger particulate quantity typical of the flue gas from refuse-fired equipment. It will normally be removed from the flue gas by a scrubber or particulate control device. Since no  $\text{NH}_4\text{HSO}_4$  is predicted in this case, the elimination of  $\text{H}_2\text{SO}_4$  is actually beneficial in reducing the potential for wet, acidic deposits at the cold end heat transfer surfaces such as economizers or air preheaters.

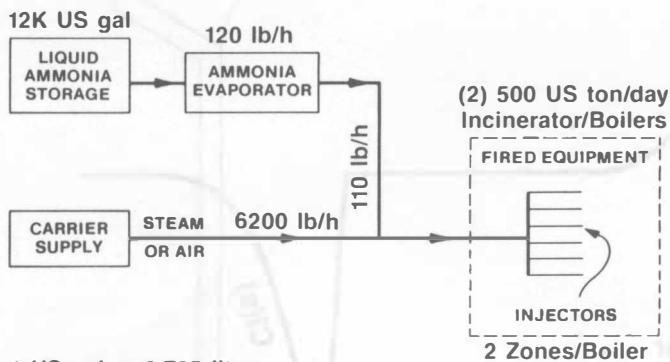
The impact of  $\text{NH}_4\text{Cl}$  formation will be a function of the type of cleanup equipment utilized and its operation. For instance, if a dry scrubber is utilized with an outlet temperature of 190°F (90°C), essentially all  $\text{NH}_4\text{Cl}$  will form and be removed in the scrubber. If the scrubber effluent is then sent to a baghouse, any residual  $\text{NH}_4\text{Cl}$  will be removed as a particulate. Ex-

perience has also shown that reduction of residual  $\text{NH}_3$  is effective in limiting  $\text{NH}_4\text{Cl}$  plume formation in plants not equipped with scrubbers [3, 12]. In most cases, predicted residual  $\text{NH}_3$  in refuse incinerators can be maintained below 10 vppm while still attaining 70% or greater  $\text{NO}_x$  removal.

#### HOW MUCH DOES IT COST?

Cost information for the improved  $\text{deNO}_x$  technology applied to refuse-fired boilers shows that the process is highly cost effective when high  $\text{NO}_x$  reduction is required.

To illustrate the cost effectiveness, investment and operating costs are provided for a 1000 tons/day municipal refuse incinerator facility. It is assumed that this plant has two trains, each combusting 500 tons/



1 US gal = 3.785 liter  
 1 lb = 0.4536 kg  
 1 US ton = 907.2 kg

FIG. 6 SIMPLIFIED THERMAL DeNO<sub>x</sub> SUPPLY SYSTEM FLOW DIAGRAM

day of refuse, and the heat is used to generate superheated steam. Untreated flue gas contains 230 vppm NO<sub>x</sub> at 12% CO<sub>2</sub> (dry), and 65% NO<sub>x</sub> removal is required.

The deNO<sub>x</sub> facilities include one 120 lb/hr NH<sub>3</sub> vaporizer, one 12k gallon liquid NH<sub>3</sub> storage tank, injectors, piping and analog instrumentation. A schematic of this equipment is shown in Fig. 6. The vaporizer is designed to provide NH<sub>3</sub> for both units at the maximum rate required, and is electrically heated. The storage tank holds sufficient ammonia to allow operation of both boilers for approximately two weeks at design load. Two zones of independently controlled injectors are provided for each boiler because of the variations in firing conditions and flue gas temperatures that can be expected when firing refuse.

As shown in Table 2, the estimated investment cost for the equipment totally erected is \$725k. Equipment cost is \$350k. Indirect cost is \$375k and includes field labor overheads, construction supervision and equipment, labor wage taxes, erection fee, engineering costs and contingency. Excluded from these costs are such items as land, owners' charges and licensing fee. Costs are on a third quarter 1985 Southern California basis.

Also shown in Table 2 is the cost effectiveness for this installation both in \$/lb (\$/kg) of NO<sub>x</sub> removed and \$/ton (\$/t) of refuse. Annualized costs are obtained by assuming a five year payout on investment and adding annual operating costs. For this system, the cost effectiveness is \$0.47/lb (\$1.03/kg) NO<sub>x</sub> removed, and the incremental cost is \$1.65/ton (\$1.82/t).

TABLE 2 INVESTMENT COST AND COST EFFECTIVENESS FOR THERMAL DeNO<sub>x</sub> APPLIED TO 1000 tons/day MUNICIPAL INCINERATOR

| Capital Investment <sup>(1)</sup> , k\$ |     |
|---|-----|
| Equipment <sup>(2)</sup>                | 350 |
| Indirect <sup>(3)</sup>                 | 375 |
| Total                                   | 725 |

| Cost Effectiveness <sup>(4)</sup>       |             |
|---|-------------|
| \$/lb (\$/kg) NO <sub>x</sub> removed = | 0.47 (1.03) |
| \$/US ton (\$/t) refuse =               | 1.65 (1.82) |

NOTES:

- Investment costs are on a third quarter 1985 Southern California basis.
- Includes equipment items identified in text.
- Includes field labor overheads, construction supervision and equipment, labor wage taxes, erection fee, engineering costs and contingency. Excluded are such items as land, owners' charges and licensing fee.
- Cost effectiveness is based on an annualized cost consisting of capital based on a 5-year payout and annual operating cost. This is divided by annual NO<sub>x</sub> reduction based on 65% NO<sub>x</sub> removal and annual tons of refuse.

Annual operating costs are shown in Table 3. These costs are based on a 100% load factor and include values for NH<sub>3</sub>, steam carrier and electric power for NH<sub>3</sub> vaporization. The operating cost per ton of refuse is \$1.25 (\$1.38/t).

## SUMMARY

Significant technological advances have been made with this deNO<sub>x</sub> process. The major benefits of these advances are a greater cost effectiveness through lower capital investment coupled with higher performance. In addition, the use of advanced analytical techniques to solve the interaction of both kinetic and engineering parameters permits the quantification of process effectiveness for a wide range of types of fired equipment and operating conditions.

The improved deNO<sub>x</sub> technology is particularly advantageous in facilities such as municipal refuse incinerators and coal-fired boilers which combust a high-ash fuel. Injection of NH<sub>3</sub> can now be accomplished in most cases without the need for internal injection grids which could be subject to fouling and corrosion/erosion damage. In addition, the need for constant carrier supply to the grid to prevent overheating is eliminated thus saving capital investment and operating expenditure. These and other advantages discussed herein for the improved deNO<sub>x</sub> process result in a high efficiency, relatively inexpensive NO<sub>x</sub> reduction process suitable for all types of stationary combustion equipment.



